



Regeneration of a sulfur-poisoned methane combustion catalyst: Structural evidence of Pd₄S formation

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ABSTRACT

Decomposition of PdSO₄, a species responsible for the deactivation of Pd-based methane combustion catalysts, was studied using a PdSO₄/Al₂O₃ model system. PdSO₄ was observed to behave differently under different reaction conditions. The decomposition of PdSO₄ under inert atmosphere probably involved only one reaction step and resulted in the formation of metallic palladium. Under H₂-containing atmosphere, the decomposition of PdSO₄ resulted eventually in the formation of Pd₄S, which is probably one of the many possible sulfur-containing palladium species that can be formed during regeneration of a sulfur-poisoned Pd-rich methane combustion catalyst. The formation of Pd₄S can provide a reasonable explanation to the threshold temperature of sulfur removal from the catalyst, as well as to the residual sulfur present in the catalyst after regeneration under reductive atmosphere. Overall, the results obtained in the study provide deeper insight into the regeneration process of Pd-based catalysts, possibly enabling development of a more efficient regeneration strategy.

1. Introduction

Biomethane is a potential, low-emission alternative for the conventional fuels used in the energy production, especially in the transportation sector. In order to fulfil the current and future emission regulations, an effective exhaust-gas aftertreatment system is essential also in the case of biomethane-fueled applications, especially due to the high greenhouse gas potential of methane. Al₂O₃-supported catalysts based on palladium have been found to be the most effective, owing to their high activity in methane combustion [1–5]. However, a major disadvantage of the Pd-rich catalysts is their vulnerability to sulfur poisoning [1,6–8], although sulfur-resistant catalyst systems have been reported lately [9]. Deactivation of the Pd-based catalysts by sulfur has often been concluded to result from the formation of PdSO₄ [6–8], although the latest results have showed that the deactivation may result from the joint effect of sulfur species and water vapor [10].

An effective catalyst regeneration strategy is essential for ensuring an adequate durability and lifetime of the catalyst system. The regeneration process of sulfur-poisoned Pd catalysts is not well understood, as the research in the field has, so far, mostly focused on improving the catalyst regeneration efficiency and only few mechanistic studies have been published [2,11–13]. The regeneration of a PdSO₄/Al₂O₃ model catalyst under oxidative conditions has been observed to occur via a two-step reaction path, resulting eventually in the formation of metallic Pd, which can be oxidized to PdO [10]. However, the

regeneration under oxidative atmosphere requires impractically high temperature (at least 650 °C) [4,10,14]. Under vacuum and reductive atmosphere, an efficient regeneration has been observed to occur at lower temperatures with respect to oxidative atmosphere [4,8,11]. Hoyos et al. have studied the regeneration mechanism of a sulfur-poisoned Pd catalyst under inert and reductive atmospheres [8]. They reported the formation of PdO under flowing nitrogen and the formation of PdS under flowing hydrogen [8]. Nevertheless, many aspects of the regeneration process are still controversial.

In this study, the regeneration of a sulfur-poisoned Pd-based methane combustion catalyst is examined under inert and reductive atmospheres. The main objective is to obtain further insight into how and why the regeneration occurs. The study is conducted by using a PdSO₄/Al₂O₃ model catalyst, enabling easier detection and quantification of the phenomena involved in the regeneration process. As already mentioned above, the formation of PdSO₄ has often been concluded to be responsible for the deactivation of Pd-based methane combustion catalysts. Hence, the stability of PdSO₄ under different reaction conditions, as well as the state of palladium after the regeneration are of special interest. The effect of temperature on the regeneration process is also studied. Herein, we provide the first structural evidence concerning the nature of palladium species formed in the decomposition of PdSO₄ under reductive atmosphere.

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2. Experimental

2.1. Preparation of the catalyst

The $\text{PdSO}_4/\text{Al}_2\text{O}_3$ model catalyst was prepared at room temperature by mixing PdSO_4 (Sigma Aldrich) into water, followed by the addition of $\gamma\text{-Al}_2\text{O}_3$ (Sasol). The mixture was stirred for 18 h to disperse PdSO_4 over Al_2O_3 . Water was removed from the mixture by evaporating first at room temperature and then at 90 °C for 1 h. The final product was a fine brownish powder having a palladium loading of 4 wt % at metallic state. Based on elemental analysis, sulfur content of the model catalyst was 0.95 wt %, which is in a good agreement with the theoretical value (1.21 wt %).

2.2. Thermal decomposition of PdSO_4 on Al_2O_3

Temperature-programmed techniques (a Quantachrome Instrument Autosorb-iQ gas sorption analyzer) were used to simulate the catalyst regeneration and to study the stability of sulfur compounds in different gas atmospheres. The instrument was equipped with a thermal conductivity detector (TCD) and a quadrupole mass spectrometer (MS), enabling identification and analysis of the gaseous reaction products. The sample size was approximately 100 mg and a cold trap immersed in an isopropanol bath (approximately –60 °C) was used to trap water formed in the reactions. Details of the temperature-programmed techniques have been presented in Table 1. O_2 consumption during TPO treatment was determined by integrating area above quantitative TCD signal. The instrument was calibrated by manually injecting O_2 pulses of known volume and by applying ideal gas law.

2.3. Characterization of the products

The sulfur content of the catalyst samples were determined using a vario MICRO cube elemental analyzer. Sulfanilamide was used for calibrating the instrument and also as a reference compound for the sulfur determinations.

The powder X-ray diffraction (PXRD) patterns of the catalyst samples were recorded in Bragg–Brentano geometry with a Bruker AXS D8 Advance diffractometer using $\text{Cu K}\alpha$ radiation and the following parameters: a measurement range (20) between 15° and 85°, a step size of 0.04° and a time per step of 10 s.

The Fourier transform infrared (FTIR) spectra of the solid samples were recorded using a Bruker Vertex 70 spectrometer equipped with a KBr beam splitter and a deuterated triglycine sulfate (DTGS) detector. The catalyst samples were finely grounded, diluted in KBr, and measured using the pressed pellet technique (a number of scans of 16 and a resolution of 2 cm^{-1}). The FTIR spectra were normalized so that the maximum absorbance of each spectrum was set to 1.0.

The specific surface area of the catalyst samples based on BET (Brunauer–Emmett–Teller) theory were determined using a Quantachrome Instrument Autosorb-iQ gas sorption analyzer. The measurements were conducted at temperature of –196 °C under liquid N_2 . Samples were pre-treated under vacuum at 350 °C for 1 h prior to

Table 1
Details of temperature-programmed techniques employed in the study.

Treatment	Atmosphere	Heating/cooling cycle	Heating/cooling rate ($^{\circ}\text{C min}^{-1}$)	Gas flow rate ($\text{cm}^3 \text{min}^{-1}$)
TPD	inert: He	25 to 1000 to 250 °C	10	20
TPR	reductive: 10 vol % of H_2 in Ar	25 to 700 to 250 °C	10	20
TPO	oxidative: 10 vol % of O_2 in He	25 to 700 to 250 °C	10	20

the measurements.

Performance and regeneration of $\text{PdSO}_4/\text{Al}_2\text{O}_3$ model catalyst (sample size of 0.2 g) under simulated exhaust gas was evaluated using a laboratory-scale reactor equipped with an on-line IR spectrometer (Gasmex™ DX4000 FTIR gas analyzer), enabling real-time characterization of the reaction gas composition. Methane conversion activities under steady-state operation were measured using the following gas composition: 2000 ppm of CH_4 , 2000 ppm of CO , 500 ppm of NO , 6% of CO_2 , 10% of O_2 , and 10% of H_2O . The gas mixture was balanced with nitrogen to give a total gas flow rate of $1180 \text{ cm}^3 \text{ min}^{-1}$, corresponding to a space velocity of $354,000 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$ through the catalyst powder. Regeneration experiments under simulated exhaust gas were conducted by temporarily replacing O_2 from the exhaust gas with N_2 in order to maintain a constant gas flow rate.

3. Results and discussion

3.1. Decomposition of PdSO_4 under He atmosphere

Decomposition of Al_2O_3 -supported PdSO_4 under inert helium atmosphere was studied using temperature-programmed decomposition (He TPD). Based on TCD and mass spectrometry data presented in Fig. 1a, the decomposition of PdSO_4 under He atmosphere was initiated approximately at 550 °C. In our previous study, the corresponding temperature in O_2 -containing atmosphere was observed to be significantly higher (800 °C) [10], indicating that PdSO_4 is destabilized in the absence of O_2 . As opposed to the decomposition of PdSO_4 under oxidative atmosphere [10], only a minor release of O_2 , before simultaneous liberation of O_2 and SO_2 , was observed in the case of He atmosphere. Thus, TPD data suggests that the decomposition of PdSO_4 under inert atmosphere may involve only a single step, differing from the reported two-step mechanism under oxidative atmosphere [10]. Nevertheless, the role of oxygen in the decomposition of PdSO_4 is still not completely confirmed.

Based on elemental analysis, the model catalyst contained only 0.06 wt % of sulfur after the He TPD treatment. A low sulfur content of the TPD-treated catalyst with respect to that of untreated $\text{PdSO}_4/\text{Al}_2\text{O}_3$ model catalyst (0.95 wt %), as well as the absence of the asymmetric stretching vibration of sulfate group at 1150 cm^{-1} [15] in the FTIR spectrum (Fig. 1b), indicated almost total decomposition of PdSO_4 under helium atmosphere. According to a PXRD study presented in Fig. 1c, palladium existed as metallic Pd after the He TPD treatment, as PXRD pattern of the TPD-treated model catalyst exhibited only signals of $\gamma\text{-Al}_2\text{O}_3$ and Pd. From the catalysis point of view, the formation of metallic Pd can be adverse due to its low activity in low-temperature methane combustion and vulnerability to sintering [16]. Previously, the decomposition of PdSO_4 under inert atmosphere and vacuum has been concluded to result mainly in the formation of palladium oxide, although PdO was not directly observed [8].

3.2. Decomposition of PdSO_4 under reductive atmosphere

Temperature-programmed reduction (TPR) technique was used to investigate decomposition of PdSO_4 on Al_2O_3 under H_2 -containing atmosphere. According to TCD and mass spectrometry data (Fig. 2a), PdSO_4 started to react under flowing hydrogen already at 250 °C. However, the release of sulfuric gases (SO_2 and H_2S), indicating decomposition of sulfur-containing palladium species, was observed to begin at surprisingly high temperature of 500 °C. The initiation temperature of PdSO_4 decomposition under H_2 -containing atmosphere was lower than that in the cases of inert and oxidative atmospheres [10]. In accordance with previous studies [8,11], the model catalyst system was found to contain some residual sulfur (0.30 wt %) after the treatment under reductive conditions. However, the absence of asymmetric stretching absorption of sulfate group at 1150 cm^{-1} in the FTIR spectrum of TPR-treated model catalyst (Fig. 2b) indicated complete

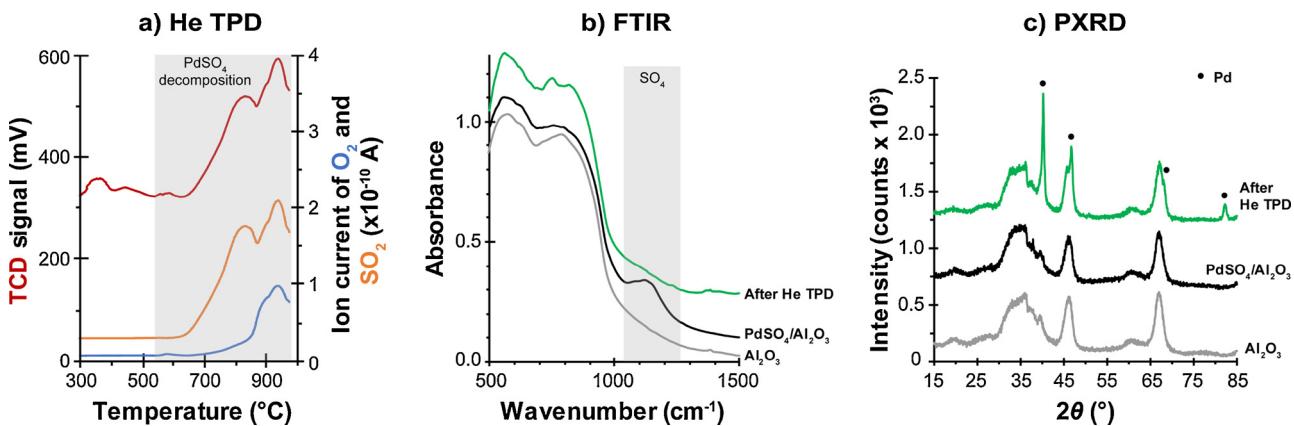


Fig. 1. a) TCD and mass spectrometry data recorded during He TPD treatment of PdSO₄/Al₂O₃ model catalyst; b) FTIR spectra and c) powder X-ray diffractograms of Al₂O₃ support and PdSO₄/Al₂O₃ model catalyst before and after the He TPD treatment. Reflections of Pd (JCPDS #46-1043) in the X-ray diffraction pattern are marked with dots (•).

reduction of PdSO₄ due to TPR treatment.

Based on PXRD data (Fig. 2c), palladium was found to exist mainly as Pd₄S after the TPR treatment, giving an explanation to the residual sulfur in the catalyst. The presence of Pd₄S phase was further supported by the experimental Pd/S molar ratio of the regenerated model catalyst (4.1), which is in a good agreement with the theoretical value of 4.0. Previously, an unsupported Pd metal film has been found to react with H₂S, resulting in the formation of Pd₄S film [17]. In addition, the synthesis of Pd₄S under reductive atmosphere from PdSO₄ anchored on carbon nanofibers [18,19], as well as from other precursors [20–22], have been reported. Xu et al. have studied H₂-assisted sulfidation of metallic palladium supported on activated carbon [23]. They concluded that different palladium sulfide phases can be selectively synthesized by controlling the reaction conditions and atmosphere. The formation of Pd₄S phase was found to predominate at 550–600 °C [23]. However, in the context of methane combustion catalyst regeneration, no reports on the formation of Pd₄S have been published.

Hoyos et al. concluded that the heating of PdSO₄ under flowing hydrogen at temperature of 400 °C resulted in the formation of palladium sulfides [8]. The formed PdS was assumed to be oxidized back to PdSO₄, although neither PdS nor PdSO₄ were directly observed [8]. In addition, the methane conversion activity of the catalyst was only slightly recovered in the process, indicating a poor regeneration efficiency [8]. Based on our TPR data (Fig. 2a), it is feasible that the heating of PdSO₄ in the presence of H₂ initially produces PdS. Nevertheless, results obtained in this study unambiguously show that Pd₄S is the palladium sulfide phase formed in a temperature range between

500 °C and 700 °C under flowing hydrogen. Different stabilities of palladium sulfide phases as a function of temperature [23] could explain the observed stepwise reaction of PdSO₄ under reductive atmosphere, as well as the detected threshold temperature (500 °C) of sulfur removal from the PdSO₄/Al₂O₃ model system. Similar threshold temperature has been previously reported also in the regeneration of a sulfur-poisoned Pd-based methane combustion catalyst [24]. However, the phenomenon has not been thoroughly explained.

3.3. Stability of Pd₄S under oxidative atmosphere

Previously, bulk Pd₄S has been reported to be unstable in the presence of O₂ at temperature above 200 °C [21]. In order to evaluate the stability of Al₂O₃-supported Pd₄S under oxidative atmosphere, the TPR-treated PdSO₄/Al₂O₃ model catalyst sample described in Section 3.2 was further examined using temperature-programmed oxidation (TPO) technique (see Fig. 3a). An uptake of O₂ was observed during the heating step of TPO treatment (50–450 °C). The molar ratio between oxygen consumed during the TPO treatment (determined on the basis of TCD signal) and palladium present in the sample (n(O):n(Pd)) was 1:1.1, indicating partial oxidation of the palladium species. In fact, PXRD data (Fig. 3c) revealed the replacement of Pd₄S with PdO and a minor amount of metallic Pd. However, the sulfur content of the model catalyst remained essentially unchanged (0.30 wt %). The residual sulfur exists likely as some sulfate or sulfite species (PdSO_x), probably as PdSO₄, which has been found to be stable under the reaction conditions used [10]. The presence of sulfate species in the model catalyst

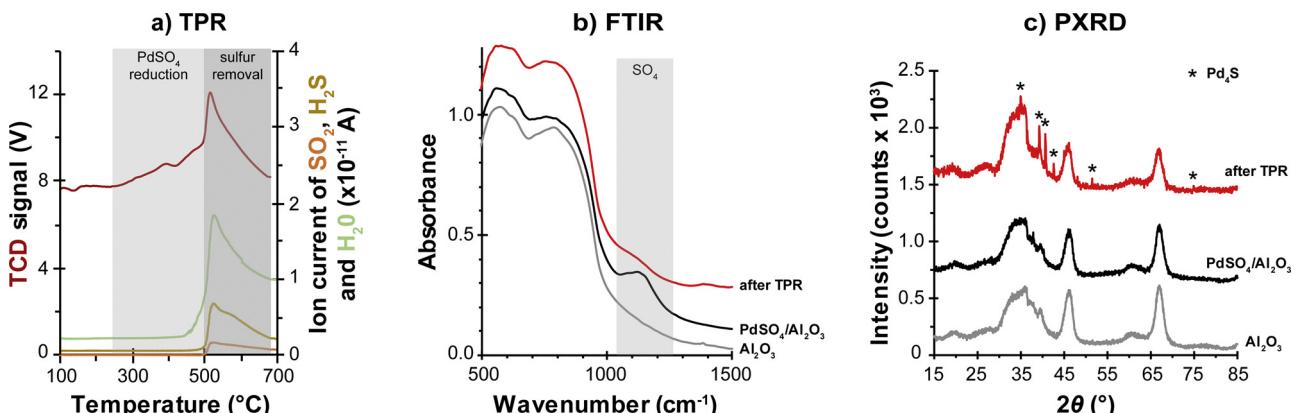


Fig. 2. a) TCD and mass spectrometry data recorded during TPR treatment of PdSO₄/Al₂O₃ model catalyst; b) FTIR spectra and c) powder X-ray diffractograms of Al₂O₃ support and PdSO₄/Al₂O₃ model catalyst before and after the TPR treatment. Reflections of Pd₄S (JCPDS #73-1387) in the X-ray diffraction pattern are marked with asterisks (*).

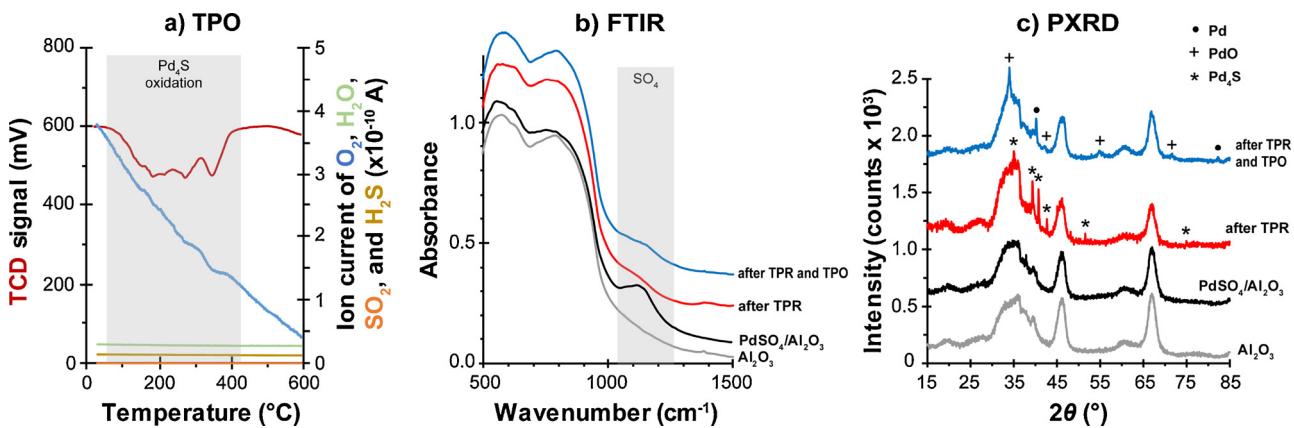


Fig. 3. a) TCD and mass spectrometry data recorded during TPO treatment of Pd-treated $\text{PdSO}_4/\text{Al}_2\text{O}_3$ model catalyst (Pd_4S on Al_2O_3); b) FTIR spectra and c) powder X-ray diffractograms of Al_2O_3 support and $\text{PdSO}_4/\text{Al}_2\text{O}_3$ model catalyst before any treatments, after TPR, and after sequential TPR and TPO treatments. Reflections of Pd (JCPDS #46-1043), PdO (JCPDS #41-1107), and Pd_4S (JCPDS #73-1387) are marked with dots (•), crosses (+), and asterisks (*), respectively.

Table 2

Summary of TPD, TPR and sequential TPR and TPO treatments of $\text{PdSO}_4/\text{Al}_2\text{O}_3$ model catalyst.

Sample	Sulfur content (wt %)	State of palladium	BET surface area ($\text{m}^2 \text{ g}^{-1}$)
fresh $\text{PdSO}_4/\text{Al}_2\text{O}_3$	0.95	PdSO_4	183
$\text{PdSO}_4/\text{Al}_2\text{O}_3$ after He TPD	0.06	Pd	202
$\text{PdSO}_4/\text{Al}_2\text{O}_3$ after TPR	0.30	Pd_4S	194
$\text{PdSO}_4/\text{Al}_2\text{O}_3$ after TPR and TPO	0.30	PdO , Pd, PdSO_x	193

after sequential TPR and TPO treatments was supported by a weak signal of sulfate group in the FTIR spectrum presented in Fig. 3b.

The most important results of TPD, TPR and sequential TPR and TPO treatments of $\text{PdSO}_4/\text{Al}_2\text{O}_3$ model catalyst have been summarized in Table 2, which includes also surface area determinations based on BET analysis. Fresh and all the treated catalyst samples exhibited a surface area typical for $\gamma\text{-Al}_2\text{O}_3$, indicating that no significant morphological changes had occurred due to any of the treatments.

3.4. Regeneration of $\text{PdSO}_4/\text{Al}_2\text{O}_3$ model catalyst under simulated exhaust gas

Methane conversion activity and regeneration of $\text{PdSO}_4/\text{Al}_2\text{O}_3$ model catalyst under simulated exhaust gas were studied at different

temperatures (Fig. 4). The regeneration cycles were conducted by temporarily replacing O_2 from the exhaust gas with N_2 . At 400 °C, only a minor release of SO_2 was observed during the regeneration cycle, resulting in only slightly increased methane conversion. In the cases of regeneration cycles at 450 °C and especially at 500 °C, a significantly higher amount of sulfur was removed from the catalyst in the form of SO_2 , with respect to the amount of sulfur released during regeneration at 400 °C. Consequently, the methane conversion activity was notably increased, indicating a more efficient regeneration of the model catalyst. Hence, the regeneration of $\text{PdSO}_4/\text{Al}_2\text{O}_3$ catalyst under realistic operation conditions occurs only at temperatures higher than 450 °C, providing further support for the threshold temperature of sulfur removal from the catalyst, which was observed in the case of H_2 TPR treatment (Section 3.2) and which has also been previously reported

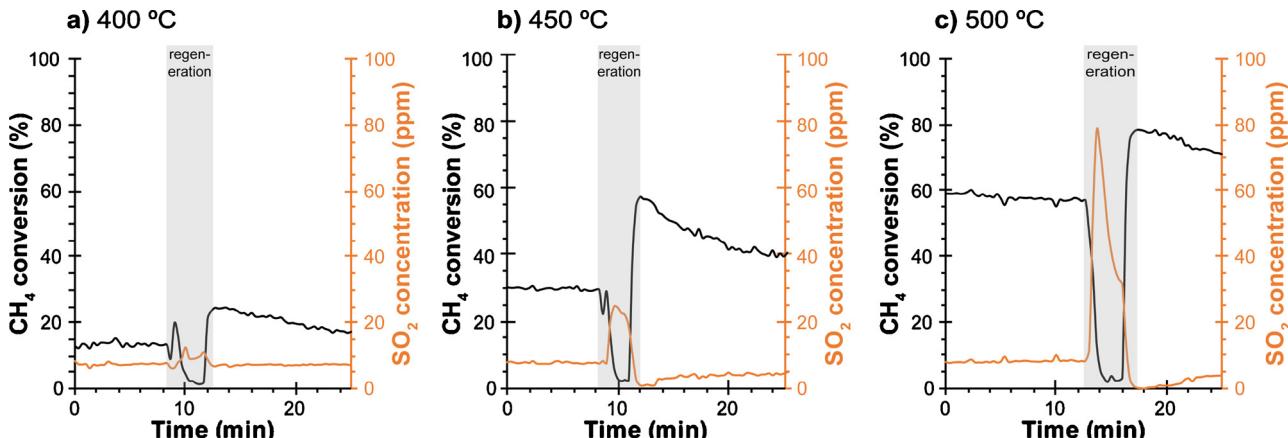


Fig. 4. Methane conversion (%) of the catalyst and concentration (ppm) of SO_2 released from the catalyst during steady-state operation and regeneration of $\text{PdSO}_4/\text{Al}_2\text{O}_3$ catalyst (sample size of 0.2 g) at a) 400, b) 450, and c) 500 °C under simulated exhaust gas containing 2000 ppm of CH_4 , 2000 ppm of CO , 500 ppm of NO , 6% of CO_2 , 10% of O_2 , and 10% of H_2O . During regeneration cycles O_2 was temporarily replaced with N_2 .

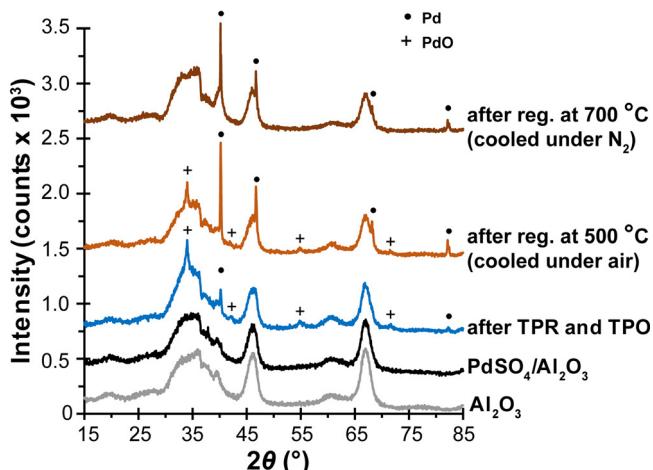
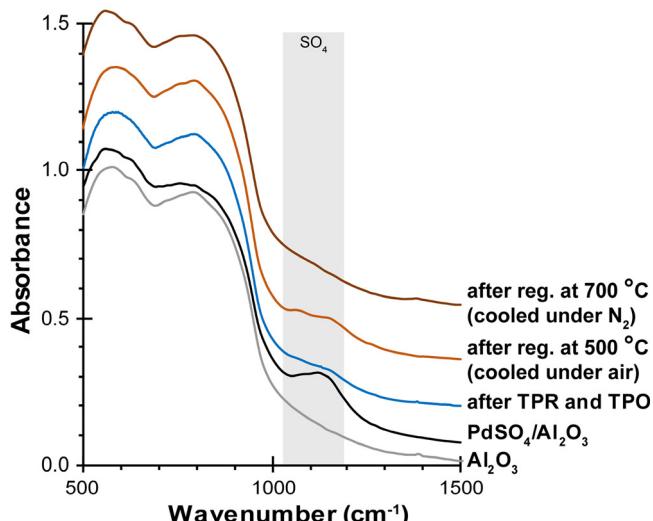
a) PXRD**b) FTIR**

Fig. 5. a) Powder X-ray diffractograms and b) FTIR spectra of PdSO₄/Al₂O₃ model catalyst after consecutive regeneration cycles under simulated exhaust gas at 400, 450 and 500 °C (cooled down under air), as well as after additional regeneration cycles at 700 °C (cooled down under N₂). PXRD pattern and FTIR spectrum of PdSO₄/Al₂O₃ model catalyst after sequential TPR and TPO treatments (see Section 3.3) have also been included for comparison. Reflections of Pd (JCPDS #46-1043) and PdO (JCPDS #41-1107) are marked with dots (•) and crosses (+), respectively.

[24].

According to a PXRD analysis presented in Fig. 5a, palladium existed mainly as Pd and PdO after consecutive regeneration cycles at 400, 450 and 500 °C under simulated exhaust gas. The catalyst sample had been cooled down to room temperature under air, resulting in partial oxidation of metallic Pd to PdO. However, a reasonably high sulfur content of the regenerated model catalyst (0.80 wt %) with respect to that of fresh PdSO₄/Al₂O₃ model catalyst (0.95 wt %) indicated that these three regeneration cycles were insufficient to remove a significant amount of sulfur from the catalyst. Moreover, the FTIR spectrum of the regenerated model catalyst (Fig. 5b) exhibited two partly overlapping absorptions (1065 and 1135 cm⁻¹) in a region typical for the sulfate group, indicating the presence of multiple sulfur containing species in the catalyst sample.

The PdSO₄/Al₂O₃ model catalyst, which already underwent regeneration cycles at 400, 450 and 500 °C, was further regenerated

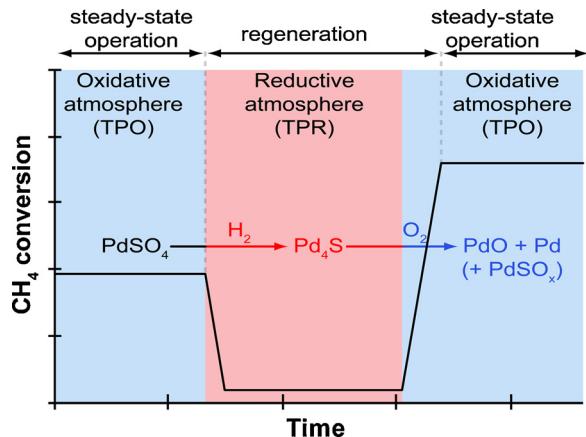


Fig. 6. Schematic presentation of the regeneration process under simulated exhaust gas.

multiple times at 700 °C in order to remove as much sulfur as possible from the catalyst. Cooling down of the catalyst to room temperature was conducted under inert N₂ atmosphere. According to elemental analysis, the model catalyst regenerated at 700 °C still contained 0.13 wt % of sulfur, indicating that even extensive regeneration cannot remove all the sulfur from the model catalyst. The low sulfur content of the model catalyst gas was further supported by the absence of the asymmetric stretching vibration of sulfate group at 1150 cm⁻¹ in the FTIR spectrum (Fig. 5b). The residual sulfur present in the catalyst provides a reasonable explanation to the observation that methane conversion activity of a sulfur-poisoned Pd/Al₂O₃ catalyst cannot be fully recovered at realistic operation conditions [2,11,13,14,24,25]. However, the regeneration under simulated exhaust gas resulted in a significantly lower sulfur content of the model catalyst compared to the sulfur content obtained by regeneration under flowing H₂ (Section 3.2), indicating importance of O₂ pulses to the overall regeneration process. On the basis of PXRD data (Fig. 5a), the model catalyst regenerated at 700 °C contained mainly metallic Pd. However, the PXRD signals were wide and partly shifted and split, suggesting structural disorder and/or a possible presence of other phases in minor amounts. PdO was not observed probably because of the inert atmosphere, under which the catalyst sample was cooled down to room temperature. Moreover, the presence of Pd₄S in catalyst samples regenerated under simulated exhaust gas could not be unambiguously detected.

The atmosphere and reactions occurring during regeneration under simulated exhaust gas are much more complex than in the cases of TPD, TPR and TPO treatments presented in Sections 3.1–3.3. Nevertheless, these simple experiments can provide important information about the overall regeneration process. As mentioned above, the catalyst regeneration under simulated exhaust gas was initiated by removing oxygen from the gas feed, resulting in virtually 0% methane conversion. In these highly rich operation conditions, H₂ is produced via steam reforming reaction [26], making the atmosphere reducing. Hence, the reaction conditions at the initial stage of regeneration cycle under simulated exhaust gas resembled those that were used in the H₂ TPR treatment (see Section 3.2). The regeneration cycle under simulated exhaust gas was finished by restoring oxygen back to the gas feed. At this point, the reaction conditions resembled those used in the TPO treatment (Section 3.3). Hence, the overall regeneration cycle under simulated exhaust gas can be considered as sequential TPR and TPO treatments (Fig. 6).

Removal of sulfur from the catalyst occurs during reductive part of the regeneration cycle. Based on our TPR results (Section 3.2), Pd₄S is at least one of the possible Pd species [23] that can be formed as PdSO₄ is reduced. However, Al₂O₃-supported Pd₄S was found to be unstable under O₂-containing atmosphere (Section 3.3). As the regeneration

cycle ends and oxygen is restored back into the gas feed, Pd_4S is converted to PdO and metallic Pd (and possibly to PdSO_x), resulting eventually in increased methane conversion activity, i.e. regeneration of the catalyst. Overall, the final regeneration products of $\text{PdSO}_4/\text{Al}_2\text{O}_3$ model catalyst under simulated exhaust gas are the same as in the case of sequential TPR and TPO treatments (PdO , Pd and PdSO_x). Pd_4S is one of the possible intermediate products that can be formed during the regeneration process.

4. Conclusions

The study revealed important aspects of the regeneration process of sulfur-poisoned Pd -rich methane combustion catalysts. PdSO_4 , a plausible cause of the catalyst deactivation, was observed to behave differently under inert and reductive atmospheres. The decomposition of PdSO_4 under inert He atmosphere occurred probably via a single-step mechanism and resulted in the formation of metallic Pd . Furthermore, PdSO_4 was found to be more unstable under inert atmosphere than under oxidative atmosphere [10]. Under flowing hydrogen, PdSO_4 reacted likely via a multi-step mechanism, resulting eventually in the removal of sulfur from the catalyst and in the formation of Pd_4S in a temperature range between 500 °C and 700 °C. The formation of different palladium sulfide phases during catalyst regeneration under reductive atmosphere could provide a reasonable explanation to the threshold temperature of sulfur removal from the catalyst (450–500 °C), as well as to the residual sulfur present in the catalyst after regeneration. Al_2O_3 -supported Pd_4S was found to be unstable under oxidative atmosphere. Consequently, Pd_4S cannot be detected after regeneration under realistic operation conditions, in which oxygen is always present after the regeneration cycle. Pd_4S can be considered as one of the many possible intermediate products that can be formed during regeneration of a sulfur-poisoned Pd -based methane combustion catalyst. Further studies are still needed to fully understand the regeneration process. The formation of Pd_4S on Al_2O_3 may be interesting also outside the context of methane combustion catalysis, as Pd_4S has been found to be a potential material for solar cell, high-temperature electrode and catalytic applications [18–21]. Overall, the results obtained in the study pave the way for a more comprehensive understanding of regeneration of Pd -based catalysts, possibly enabling more rational development of methane combustion catalysts and regeneration strategies.

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